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Specific heat of superconducting κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ near T_c [where BEDT-TTF is bis(ethylenedithio) tetrathiafulvalene]

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High-resolution specific-heat measurements on a small (0.2 mg) single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in magnetic fields up to 5 T reveal a jump ΔC at T_c. Comparison with $\gamma = 34$ mJ/mol K^2 derived from Pauli paramagnetism yields $\Delta C/\gamma T_c = 1.50 \pm 0.15$, within experimental error of the BCS value of 1.43. Application of a magnetic field broadens the transition but depresses it only slightly: $-H_{c2}' = 16$ T/K for H parallel to the planes, 0.75 T/K perpendicular. These very large values are, respectively, factors of 7 and 4 times higher than reported from magnetoresistance data, suggesting that flux-flow resistance obscures T_c in magnetoresistance measurements, much as it does in the ceramic high-T_c materials. No evidence is found for the presence of an anomaly near 4 K, as observed in proton NMR relaxation rates.

The family of Bechgaard salts offers an unusually rich variety of phenomena,[1] including field-induced spin-density waves, pressure-induced superconductivity, and recently zero-pressure high-temperature superconductivity. κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is superconducting[2] below $T_c \approx 10$ K, a remarkably high temperature for a material with such large resistivity in the normal state (10^{-2} Ω cm, compared to 10^{-5}–10^{-4} Ω cm for high-T_c perovskite materials). The crystal structure is quasi two dimensional and the electrical transport properties and superconductivity parameters (σ, ξ, H_{c2}) are correspondingly very anisotropic.[3–7] Recent muon-spin-rotation (μSR) measurements[8] in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ are consistent with BCS pairing.

We report high-resolution specific-heat measurements in large magnetic fields which reveal a jump on cooling through T_c that agrees with the BCS value to within 5%. The behavior of the jump as a function of applied fields bears a strong resemblance to that observed in the high-T_c perovskite materials. Furthermore, our measurements of specific-heat and microwave absorption shed light on several unexplained observations in this material that have provoked imaginative speculations:[4,9] the phase diagram of H_{c2} vs T has a peculiar upwardly concave curvature[6,7] for H oriented perpendicular to the planes, and the proton NMR relaxation rate[4,7] exhibits a strong peak around 5 K.

The κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystals used in the present study (typical dimensions $2 \times 1 \times 0.1$ mm^3) were grown according to the general procedure of Urayama *et al.*[2] Recrystallized BEDT-TTF (20 mg) was dissolved in the anode compartment of an electrochemical H cell containing filtered 1,1,2-trichloroethane electrolyte solution (60 ml), under an atmosphere of argon. The electrolyte mixture was prepared by stirring KSCN (49 mg), CuSCN (61 mg), and 18-crown-6 (264 mg) in dry, distilled, 1,1,2-trichloroethane (100 ml) overnight under argon. Crystal growth was complete in 2–3 weeks. The BEDT-TTF cations form a relatively isotropic, two-dimensional conducting layer in the *b-c* plane, while the Cu[NCS]$_2$ anions are arranged in one-dimensional chains along the *b* axis, forming insulating layers between the BEDT-TTF molecules. The *b-c* plane is parallel to the largest faces of the crystals.

The heat capacity of a crystal, weighing typically 0.2 mg, was measured with the modulated-bath technique[10] which allows resolution of a part in 10^3 and accuracy of ~5% on small samples with negligible addenda. The advantage of being able to use small samples is, of course, that they are usually more uniform and homogeneous than larger samples. The sample is attached with a minute amount of silver paste, at the center of a large face, to the junction of a Chromel-Constantan thermocouple (50-μm-diam wire, 1 mm long). The other ends of the thermocouple wires are anchored to Au electrical pads on a small sapphire substrate, the temperature of which can be modulated by, typically, 0.1 K p-p. If the modulation frequency is chosen properly (~0.1 Hz, in this case), the amplitude of the ac thermocouple voltage is proportional to the heat capacity of the sample plus addenda. For the present samples and thermocouple, the addenda are estimated to contribute approximately 2% to the heat capacity of the sample and have, therefore, been ignored in the data reduction. Samples were screened for sharp T_c by microwave absorption,[11] which showed a sharp onset at ~9.5 K in the best samples. Data were taken on several samples, with essentially identical results.

The specific heat in zero applied magnetic field is shown in Fig. 1. Close examination reveals a bump at ~9 K on an otherwise smoothly rising curve. The overall behavior agrees roughly with previous data in zero magnetic field.[12] The noise level is higher at temperatures above 10 K than below because of the decreasing sensitivity of the thermometer. The anomaly can be observed more readily by plotting C/T, as in Fig. 2. Magnetoresistance studies[6,7] suggest that T_c decreases by at least 5 K in an applied magnetic field of several Tesla oriented perpendicular to the bc plane, so that data taken in $H = 5$ T should serve as a measure of the background (phonons plus normal electrons), at least down to $T = 5$ K. Such data are also shown in Fig. 2. The difference between the two sets of data therefore gives the change in the electronic specific heat

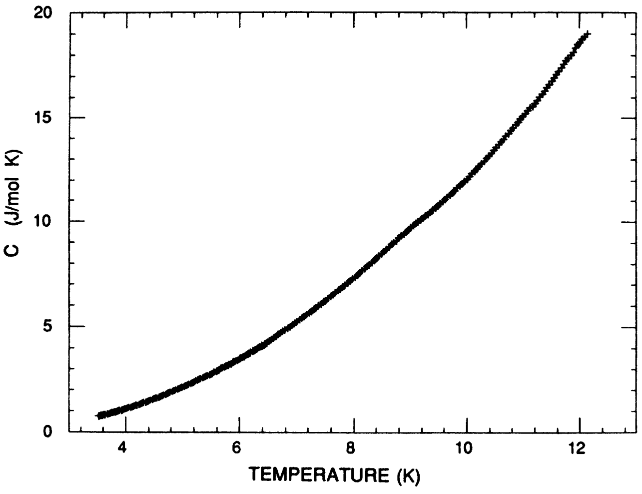

FIG. 1. Specific heat C of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in zero applied magnetic field.

due to the superconductivity. This difference is plotted in Fig. 3(a) [3(b)] for the magnetic field lying perpendicular (parallel) to the b-c plane. A prominent peak is observed for $H=0$, which can be approximated with the BCS function[13] for the specific-heat anomaly at T_c. The sharply peaked curve in Figs. 3(a) and 3(b) is the BCS function for $T_c=9.4$ K, assuming an electronic $\gamma=36$ mJ/mol K^2. Smearing the transition with a Gaussian distribution of T_c with a half width of 0.5 K yields the smooth curve in Figs. 3(a) and 3(b), which is a good approximation to the zero-field data. This model can be compared with the Sommerfeld constant derived from the Pauli paramagnetism,[5] $\gamma=34$ mJ/mol K^2, so that the BCS relation $\Delta C/\gamma T_c=1.43$ is followed to within 5%, which is well within our overall accuracy for ΔC, conservatively estimated at ±10%. This result, therefore, is in good agreement with the recent μSR measurements.[8]

The effect of a magnetic field in this organic superconductor, however, is unlike that in traditional type-II superconductors, in that the anomaly is not simply shifted to lower temperature as the field is increased. Rather, the transition is broadened and depressed, with the upper end of the transition remaining roughly fixed in temperature. Because of this behavior, which resembles that observed in YBa$_2$Cu$_3$O$_7$,[14,15] it is difficult to know what temperature to choose as T_c. Nevertheless, if we choose the midpoint of the negative-slope region as T_c, we obtain (Fig. 4) an upper critical-field slope of $H_{c2}'=dH_{c2}/dT=-0.75$ T/K, for H oriented perpendicular to the b-c plane. This large value is only a factor of 8 smaller than $H_{c2}'=-6$ T/K observed[15] in YBa$_2$Cu$_3$O$_7$, using the same definition of T_c. Previous estimates of $H_{c2}(T)$ based on magnetoresistance studies[6,7] are included in Fig. 4; these show a slope near T_c of $H_{c2}'=-0.15$ T/K, or four times lower than determined here from the specific-heat data. Similar behavior is observed with the field oriented parallel to the bc plane. For the parallel orientation, H_{c2}' is extremely large: -16 T/K. This is a factor of 7 larger than obtained from magnetoresistance data (not shown).

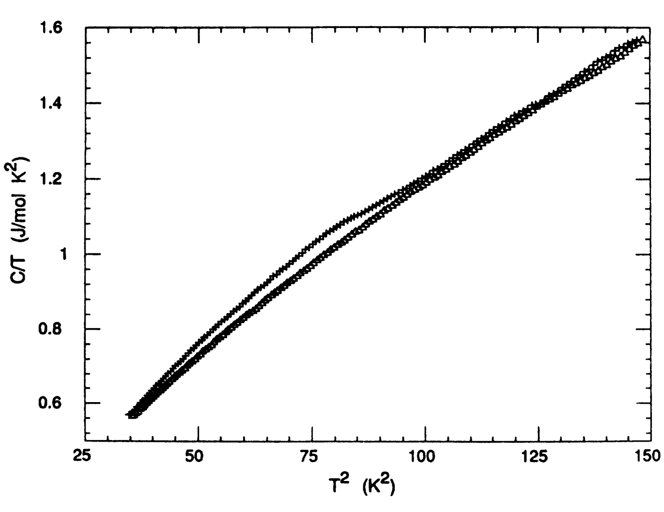

FIG. 2. C/T vs T^2 for applied fields of 0 (+'s) and 5 T (Δ's) oriented perpendicular to the b-c plane.

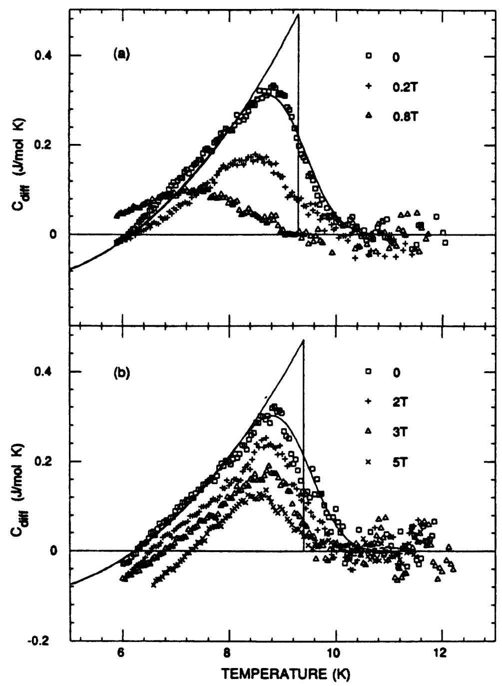

FIG. 3. (a) Specific-heat difference $\Delta C=C(H_\perp)-C(H_\perp=5$ T) for $H_\perp=0$, 0.2, and 0.8 T lying perpendicular to the b-c plane. (b) Specific-heat difference $\Delta C=C(H_\parallel)-C(H_\perp=5$ T) for $H_\parallel=0$, 2, 3, and 5 T lying in the b-c plane. The data for $H_\perp=5$ T (Fig. 2) serve as a background (phonons plus normal electrons), since $H_\perp=5$ T is strong enough to suppress T_c to below ~3 K (Fig. 4).

The magnitude of the specific-heat jump can be used to calculate the slope of the thermodynamic critical field, H_c', by means of the thermodynamic relation: $\Delta C/T_c=-V(H_c')^2/4\pi$, where V is the molar volume. We find $H_c'=-112$ Oe/K. Using this value and the relation $H_{c1}'=(H_c')^2(\ln\kappa+0.5)/H_{c2}'$, together with reasonable estimates[3] for κ ($\kappa_\perp=20$ and $\kappa_\parallel=100$), we calculate $H_{c1\perp}'=-6$ Oe/K and $H_{c1\parallel}'=-0.4$ Oe/K. These values compare quite well with -5 and -0.1 Oe/K, respectively, from direct magnetic measurements.[3] The present

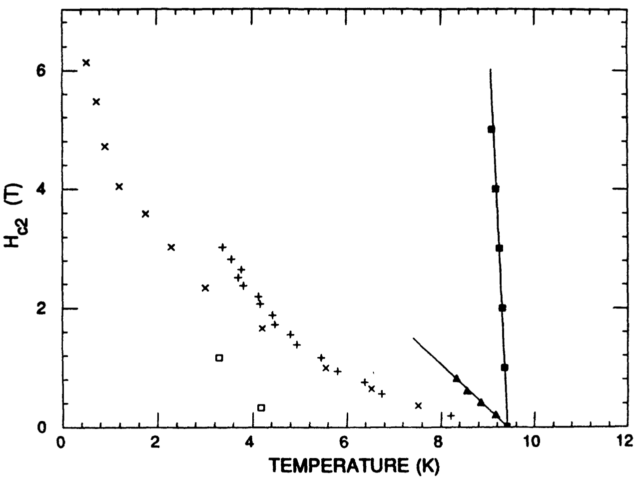

FIG. 4. Phase diagram determined from the present measurements of specific heat with the applied field parallel (■'s) and perpendicular (▲'s) to the *b*-*c* plane. Also shown are data (×'s and +'s) for the perpendicular orientation based on magnetoresistance data (Refs. 6 and 7). The □'s near $T=4$ K locate the peak of the anomalously high proton relaxation rate observed in NMR (Refs. 4 and 7).

specific-heat measurements are therefore consistent with magnetic measurements of H_{c1}'. Since the latter are insensitive to whether the bulk of the sample is in the superconducting state, this consistency implies that the specific-heat sample is a bulk superconductor. (The Meissner effect is not such a conclusive test for bulk superconductivity.[16])

The upward curvature of the magnetoresistance-based estimate of H_{c2} in Fig. 4 is unusual for H_{c2} vs T, and has been interpreted in various ways—for example, as evidence for dimensional crossover,[7] or a structural phase transition.[9] In light of the steeper slope of the present measurements and the similarities of the magnetoresistance data to that found in some of the high-T_c materials,[17,18] we argue that the magnetoresistance is dominated by flux-flow resistance and that the true T_c is much higher than given by the criterion of, for example, one half of the normal-state resistance. This would eliminate the upward curvature of the critical-field curve.

The open squares in Fig. 4 near 5 K indicate the locations of anomalously high relaxation rates measured[4,7] in NMR of the hydrogen atoms near the $\mathrm{Cu(NCS)_2}$ layers. We see no large anomaly in the specific heat in this range of field and temperature. We caution that the anomaly might be associated with the presence of some unidentified second phase in the NMR samples. With microwave absorption measurements,[11] we have observed almost complete loss of superconductivity as single crystals are broken up into ~10-μm-diam grains.[19] With such high sensitivity of the superconducting state to mechanical stress, the condition of the polycrystalline NMR samples is open to question. Further NMR experiments are recommended using well-characterized single crystals, both before and after pulverization.

There appear to be, therefore, several interesting similarities between κ-$\mathrm{(BEDT\text{-}TTF)_2Cu(NCS)_2}$ and high-T_c superconductors: the extremely high values of H_{c2}' and the behavior of the specific-heat anomaly in a magnetic field. At this point it is not known whether these similarities are due to a common underlying mechanism for superconductivity or to the similar quasi-two-dimensional structure. The more traditional behavior observed[16] in the cubic, 30-K superconductor $\mathrm{Ba_{0.6}K_{0.4}BiO_3}$ would argue in favor of the dimensionality being the important factor.

Note added in proof. Very recent measurements [B. Andraka *et al.*, Phys. Rev. B **40**, 11 345 (1989)] of the specific heat of similar material at higher magnetic fields and lower temperatures than were available for the present work provide a direct determination of the normal-state electronic specific heat: $\gamma=25\pm3$ mJ/mol K^2. Using that value, rather than the one derived from Pauli paramagnetism, with the present value of ΔC, yields $\Delta C/\gamma T_c=2.0\pm0.3$, suggesting intermediate-to-strong rather than weak coupling.

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